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V. Polymer Reaction Engineering

Free Radical Polymerization in Ionic Liquids – Solvent Influence of New Dimension

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Summary: For the free radical polymerization of polar monomers which are soluble in ionic liquids (ILs) an extraordinary strong solvent effect can be observed. The solvent influence of the ILs leads to a strong enhancement of the polymerization rate and extremely high, mostly broadly distributed molecular weights. The experimentally determined very high propagation rate coefficient k_p and the reduction of the activation energy of propagation E_A can be explained by H-bonds between both the monomer molecules and the growing radical chains and the cations and anions of the ILs. The high viscosity of the ILs themselves as well as the increase of the viscosity during the polymerization process are responsible for the high molecular weights and the mostly high polydispersities. The systematic variation of the rate constants of propagation k_p and termination k_t using microwave reactor, IL/conventional organic solvent mixtures and increased reaction temperatures is studied.

Keywords: free radical polymerization; H-bonds; ionic liquids; microwave; solvent influence

Introduction

Ionic liquids (ILs) are a new class of solvents which exclusively consist of ions. The melting point of ILs is considerably below 100 °C – in dependence on the incorporated ions they are often already liquid at room temperature (RTILs). The ILs mostly consist of a bulky organic cation like imidazolium, pyridinium, ammonium and phosphonium ions and a complex counterion like hexafluorophosphate anion (PF_6^-) and the tetrafluoroborate anion (BF_4^-). An advantage of the ILs is the great range of variation of their properties which result from the combination of different anions and cations.

The ILs have extraordinary solvent properties which can lead to an increase of reactivity and selectivity. Numerous investigations showed that ILs can be used instead of conventional organic solvents for many reactions like e.g. catalytic reactions.[1]

ILs show some characteristic chemical and physical properties like high polarity, high thermal stability, a large liquid range, very different water solubility and no or only a low vapor pressure below the decomposition temperature.

A relatively new application of ILs is their use for the free radical polymerization as an alternative for organic solvents. The number of publications concerning the free radical polymerization in ILs still is rather limited, cf. e.g.[2–26]

The strong enhancement of the overall polymerization rate r_p and the strongly increased molecular weights that are described for most of the polymerizations investigated so far, exceed the previously discussed solvent influence on the free radical polymerization.

Besides the increase of k_p,[2–4] the reduction of the rate of termination and therefore a decrease of k_t must be considered to explain the strong solvent influence. In[3] viscosity measurements of

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the IL reaction mixtures were carried out. The authors can find a correlation between the increasing viscosity of the reaction mixture and the decreasing termination rate coefficient k_t and the increasing IL concentration.

Besides the homopolymerization of methacrylates,[2–17,27] styrene (St),[5–7] acrylates,[18] 2-hydroxyethyl methacrylate,[6–8] vinyl acetate,[7,8] 1-vinyl imidazole,[8] acrylonitrile (AN)[7,19,20,27] in *N*,*N*-dialkyl imidazolium salts with [PF_6^-], [BF_4^-] und [$N(SO_2CF_3)_2^-$] as anions the free radical copolymerizations of methyl methacrylate (MMA) with St (in [BMIM]PF_6)[22,23] and with AN,[14,20] of a highly zwitterionic methacrylate with butyl methacrylate (BuMA),[21] of AN with St[13,24,25] and methyl acrylate (MA)[25] were investigated. The results show that the homopolymerization and copolymerization in ILs, particularly on the basis of 1,3-dialkyl substituted imidazoles, lead to high conversions and strongly increased molecular weights. Review articles which also describe controlled radical polymerizations in ILs are in.[18,26]

The focus of this work is the investigation of the solvent influence of the IL 1-ethyl-3-methylimidazolium ethylsulfate ([EMIM]$EtSO_4$) on homo- and copolymerizations of AN and *N*-phenyl maleimide (NPI) respectively with St and methacrylates. In this context it has to be examined how both the enhancement of the rate of polymerization and the molecular weights are influenced by the variation of the solvent viscosity as well as by microwave irradiation. The viscosity of the solvent is dependent on the IL concentration and the reaction temperature.

Experimental Part

The monomers styrene (St), acrylonitrile (AN), methyl methacrylate (MMA), glycidyl methacrylate (GMA) and hydroxypropyl methacrylate (HPMA) were distilled under vacuo to remove inhibitors and *N*-phenyl maleimide (NPI) was recrystallized from methanol before use. The solvents 1-ethyl-3-methylimidazolium ethylsulfate [EMIM]$EtSO_4$ (ECOENG^{TM} 212, Solvent Innovation GmbH), dimethyl formamide (DMF), methanol (MeOH) were used as received. The initiators 2,2′-azobisisobutyronitrile (AIBN) und benzoyl peroxide (BPO) were recrystallized before use. ***Reaction Conditions***: Monomers (1.5 g) and initiator (0.05 g AIBN or BPO) were weighed into ampoules and 6 mL of the solvent ([EMIM]$EtSO_4$, methanol, DMF or a [EMIM]$EtSO_4$/DMF mixture) were added. After purging the ampoules with nitrogen for 5 min they were sealed and the reaction was started in a preheated heating block or in a microwave reactor. The polymerization was carried out at different reaction temperatures (25 to 80 °C) and at different IL concentration in a [EMIM]$EtSO_4$/DMF solvent mixture, a temperature of 60 °C was used. The polymerization was stopped by fast cooling. The copolymerization behavior of St/AN, MMA/NPI and methacrylates/AN was investigated at 60 °C varying the comonomer mixture from 0 to 100 mol-% of AN and NPI respectively in steps of 10 mol-%.

The ***microwave*** experiments were performed in a multimode microwave reactor with fiber-optic temperature control (microPREP 1500, MLS GMBH MIKROWELLEN LABORSYSTEME). The microwave power was adjusted to a temperature of 60 °C. The temperature was measured inside the reaction mixture.

The ***viscosity*** in dependence of the IL concentration (vol.-%) in a [EMIM]$EtSO_4$/DMF solvent mixture and the temperature was measured using a Bohlin Gemini cone-plate rheometer (MALVERN) at 20 to 60 °C with a constant shear stress of 5 Pa.

The measurement of the ***molecular weight distributions*** (MWDs) was carried out on a SEC system WATERS 510 in tetrahydrofurane (THF) at 25 °C using poly(styrene) and poly(methyl methacrylate) standards.

The ***rheological investigations*** were carried out on the Dynamic Analyzer RDA II (RHEOMETRICS SCIENTIFIC) with plate-plate geometry.

For the detection of the copolymer composition the content of C, H, N, O was determined using the ***elemental analysis*** VarioEL (ELEMENTAR ANALYSE-SYSTEME GmbH). The calibration was carried out with acetanilide and benzoic acid.

A FTS 700-spectrometer from Biorad equipped with a photoacoustic measuring cell from MTEC was used for ***FTIR-PAS measurements*** with helium as inert gas (in the range 400 cm^{-1} to 4000 cm^{-1}.

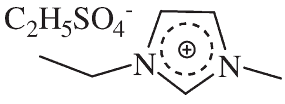
Results and Discussion

Homo- and Copolymerizations in ILs

In this work the ionic liquid [EMIM]EtSO$_4$ (cf. Scheme 1) was mostly used because it is already available in larger quantities due to its industrial production and its proved further toxicological harmlessness.[28]

Investigations on the solvent influence on the free radical polymerization require the solubility of the monomers in the IL. In[21] it is shown exemplarily for butyl methacrylate that due to elongation of the alkyl chains of the cation of the IL the monomer solubility and therefore an accelerated polymerization and a higher conversion can be achieved. Figure 1 shows the extremely strong solvent influence by comparison of the conversion versus time dependency and the time dependent molecular weight distributions (MWDs) of the free radical polymerization of methyl methacrylate (MMA) in [EMIM]EtSO$_4$ and DMF.

Considering our investigations in[4,29] we can conclude that the interactions with polar ILs increase the reactivity of the monomers and at the same time are responsible for the decrease of the activation energy of propagation which results in increasing propagation rate coefficients k_p. The k_p values we measured for MMA in [EMIM]EtSO$_4$ are 4 times higher than those measured for the bulk polymerization of MMA.[4] It has to be taken into account that not only k_p is responsible for the time dependent development of the MWDs and the length of the polymer chains but also the termination rate coefficient k_t is of extraordinary importance. Most ILs are highly viscous liquids ($\eta_{[EMIM]EtSO4} = 100.3$ mPa · s and in contrast $\eta_{DMF} = 0.95$ mPa · s at 20 °C) which means that the polymerization is already started with reduced k_t values and therefore right from the beginning of



Scheme 1.
1-Ethyl-3-methylimidazolium ethylsulfate ([EMIM] EtSO$_4$).

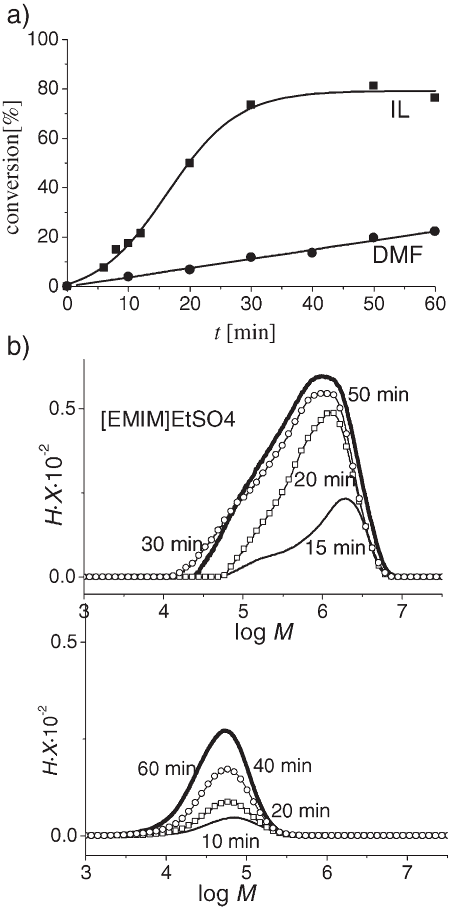


Figure 1.
a) Conversion-time dependency of the free radical MMA polymerization in [EMIM]EtSO$_4$ (■) and DMF (●), b) time dependent, conversion standardized molecular weight distributions in [EMIM]EtSO$_4$ and DMF.

the reaction very long polymer chains are formed. As long as the produced polymers are soluble in the IL the viscosity increases with increasing conversion and k_t constantly decreases and therefore the chain lengths dramatically enlarge. In our former investigations[13,14,24] we described the following polymers to be soluble in [EMIM]EtSO$_4$: poly(methyl methacrylate) (PMMA), poly(acrylonitrile) (PAN), poly(methacrylonitrile) as well as poly (hydroxylpropyl methacrylate-*co*-acrylonitrile), independent of the copolymer composition. The molecular weights of these polymers are extraordinary high. In contrast, most of the other homo- and copolymers we studied precipitate when conversions of 5 to 15% are reached.

Table 1.
Brutto polymerization rate (r_p) of the free radical polymerization of St, AN, MMA, HPMA and GMA in [EMIM]EtSO$_4$ and MeOH, reaction conditions: 1.5 g Monomer, 0.05 g (3.3 wt.-%) AIBN, $T = 60$ °C.

Monomers	$r_{p,IL}$ [%/h]	$r_{p,MeOH}$ [%/h]	$r_{p,IL}/r_{p,MeOH}$
St	5	3	1,7
AN	75	8	9.4
MMA	145	23	6.3
HPMA	396	39	10
GMA	700	21	33

In Table 1 the polymerization rates r_p of the homopolymerizations of St, AN, MMA, HPMA and GMA, carried out either in the IL [EMIM]EtSO$_4$ or in methanol (MeOH) as well as the ratios of the polymerization rates $r_{p,IL}/r_{p,MeOH}$, are summarized. With increasing polarity of the monomer the solvent influence increases.

In Figure 2 the brutto polymerization rates of the St/AN, HPMA/AN, GMA/AN, MMA/AN and MMA/NPI copolymerizations are depicted in dependence of the acceptor fraction (AN, NPI) in the monomer mixture. The comparison of the results summarized in Table 1 and Figure 2 leads to the result that the r_p values of the copolymerizations are located between

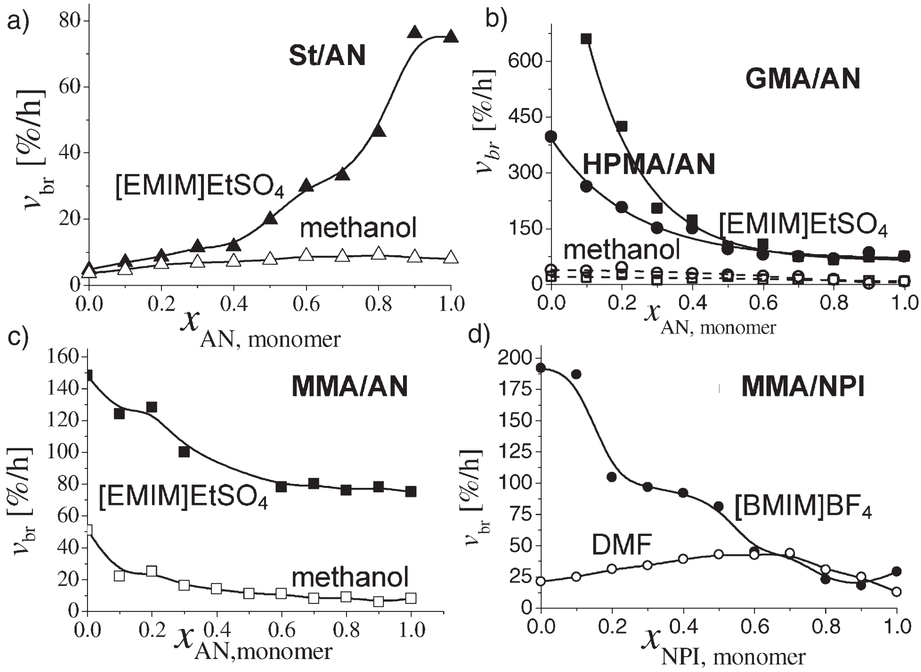


Figure 2.
brutto polymerization rates (r_p) in [EMIM]EtSO$_4$ and MeOH in dependence of the AN ($x_{AN,monomer}$) (a, b, c) or the NPI fraction in the comonomer mixture ($x_{NPI,monomer}$) (d).

those of the homopolymerizations. Since the influence of the IL on the polar AN is significantly higher than on the unpolar St. Since the solubility of the copolymers in the IL increases with increasing AN fraction in the comonomer mixture the highest polymerization rate can be found for St/AN (10/90 mol-%). The increase of the molecular weights follows the same trend (Figure 3a).

The molecular weights of the methacrylate copolymers with high AN ratio produced in ILs can not be analysed via SEC analysis because they are insoluble in THF as well as in DMF. Concerning the GMA/AN and the HPMA/AN system the insolubility of the resulting copolymers is enforced by chemical and physical crosslinking, respectively. For MMA/AN entanglement networks of the long polymer chains can be detected by rheological measurements like it is depicted for MMA/AN (80/20 mol-%) in Figure 3b. As it is typical for entanglements, the storage modulus G' and the loss modulus G'' of P(MMA-*co*-AN) synthesized in [EMIM]EtSO$_4$ are independent of the frequency for $\omega < 10^1$ rad $\cdot$ s^{-1}. This behavior cannot be found for the copolymers produced in methanol.

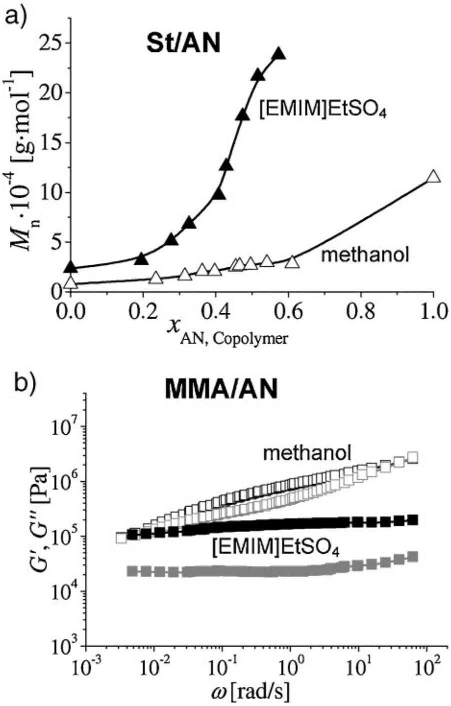


Figure 3.
a) St/AN: number average molecular weights M_n in dependence on $x_{AN,copolymer}$, calibration with poly (styrene) standards, conversion: 2-6%, $T = 60\,°C$; b) storage (G') and loss modulus (G'') of P(MMA-co-AN) (20 mol-% AN in the monomer feed) synthesized in [EMIM]EtSO$_4$ (G': ■, G'': ▨) and MeOH (G': □, G'': □) in dependence on the frequency ω.

The reactivity ratios (r_1 and r_2) for the copolymerizations carried out in [EMIM]EtSO$_4$ which were calculated via the method of KELEN and TÜDÖS[30] are summarized in Table 2 in comparison to the r values received from the reactions in conventional organic solvents.

The copolymer compositions that were determined for the polymerizations in IL as well as in methanol do not significantly differ from each other. It can be seen that the higher error margins can be obtained for the products received from the polymerizations in IL which is due to problems during the polymer purification. The agreement of the reactivity ratios of the polymerizations in IL with those of the copolymerizations performed in organic solvents (literature and own data) demonstrates that the IL does not change the copolymerization behavior in the examined systems

Table 2.
r-values of the MMA/St, St/AN, methacrylates/AN und MMA/NPI copolymerizations.

Systems	[EMIM]EtSO$_4$	Literature[31,32]
MMA/St	$r_{St} = 0{,}35 \pm 0{,}06$ $r_{MMA} = 0{,}42 \pm 0{,}06$	$r_{St} = 0{,}517$ $r_{MMA} = 0{,}42$
St/AN	$r_{AN} = 0{,}10 \pm 0{,}02$ $r_{St} = 0{,}38 \pm 0{,}04$	$r_{AN} = 0{,}04 \pm 0{,}01$ $r_{St} = 0{,}41 \pm 0{,}05$
MMA/AN	$r_{AN} = 0{,}20 \pm 0{,}12$ $r_{MMA} = 1{,}68 \pm 0{,}34$	$r_{AN} = 0{,}16 \pm 0{,}06$ $r_{MMA} = 1{,}24 \pm 0{,}11$
GMA/AN	$r_{AN} = 0{,}12 \pm 0{,}12$ $r_{GMA} = 0{,}90 \pm 0{,}20$	$r_{AN} = 0{,}14$ $r_{GMA} = 1{,}32$
HPMA/AN	$r_{AN} = 0{,}36 \pm 0{,}03$ $r_{HPMA} = 3{,}36 \pm 0{,}99$	–
MMA/NPI[a)]	$r_{NPI} = 0{,}15 \pm 0{,}09$ $r_{MMA} = 1{,}33 \pm 0{,}18$	$r_{NPI} = 0{,}16 \pm 0{,}05$ $r_{MMA} = 1{,}42 \pm 0{,}09$

[a)] in [BMIM]BF$_4$.

Solvent Influence – Rate coefficients k_p and k_t

The extraordinary solvent influence that can be observed for polar monomers in particular can basically be explained by the rate constants of propagation k_p and termination k_t.

Influence of k_p

Using *pulsed laser polymerisation* (PLP) technique the enhancement of the propagation rate coefficient k_p with increasing IL concentration was quantified by Haddleton et al. for the MMA polymerization carried out in 1-butyl-3-methylimidazolium hexafluorophosphate ([BMIM]PF_6)[2,3] and by us for the MMA and GMA polymerization performed in the ILs [BMIM]PF_6, 1-butyl-3-methylimidazolium tetrafluoroborate ([BMIM]BF_4), [EMIM]$EtSO_4$ and 1-ethyl-3-methylimidazolium hexylsulfate ([EMIM]$HexSO_4$).[4] Concerning the polymerizations in [BMIM]PF_6, [BMIM]BF_4 and [EMIM]$EtSO_4$ no significant differences for k_p could be found. The k_p values for MMA are about 4 times higher and for GMA about 2 times higher than those reported for the bulk polymerization. On the basis of the temperature dependence of k_p for polymerization of MMA and GMA[2–4] in ILs a reduced activation energy E_A of the propagation step can be determined. The ARRHENIUS parameters (A, E_A) for the MMA and the GMA bulk polymerization as well as for their solution polymerization with 80 vol.-% [BMIM]PF_6, [BMIM]BF_4 or [EMIM]$EtSO_4$ in the reaction mixture and the resulting k_p values for $T = 40\,°C$ are summarized in Table 3.

Specific interactions based on H-bonds between either the cations or the anions of the ILs and the monomer molecules as well as the chain ends of the growing polymer radicals can explain the increase of k_p and the reduction of E_A. An explicit evidence for this assumption is the shift of the valence vibration of the C=O bond in the FTIR spectra of MMA and GMA dissolved in different ILs measured at room temperature (Table 4). The absorption peak maxima are shifted to lower wavenumbers.

This shift of ν_{max}(C=O) is due to polar interactions like H-bonds between the monomers and the ILs and can directly be correlated with the increase of k_p and the decrease of E_A. The difference in the ν_{max}(C=O) values (5 cm^{-1}) of the pure

Table 3.
Arrhenius parameters A and E_A and the resulting $k_{p,40\,°C}$ values for the solution polymerization of MMA and GMA in [BMIM]BF_4,[BMIM]PF_6 or [EMIM]$EtSO_4$[4] as well as for the bulk polymerization.[34]

Monomer	Solvent	IL fraction [vol.-%]	$A \cdot 10^{-6}$ [$L \cdot mol^{-1} \cdot s^{-1}$]	E_A [$kJ \cdot mol^{-1}$]	$k_{p,40\,°C}$ [$L \cdot mol^{-1} \cdot s^{-1}$]
MMA	[BMIM]PF_6 [BMIM]BF_4	20	1.9	18.1	1843
MMA	bulk	100	2.7	22.4	490
GMA	[BMIM]BF_4 [EMIM]$EtSO_4$	20	3.7	19.5	2067
GMA	bulk	100	6.2	22.9	937

Table 4.
Peak maxima ν_{max}(C=O) of the stretching vibration of the carbonyl group for MMA and GMA in IL solutions with 10 vol.-% monomer.

IL	IL fraction [vol.-%]	ν_{max}(C=O) MMA [cm^{-1}]	ν_{max}(C=O) GMA [cm^{-1}]
–	–	1726	1721
[EMIM]$HexSO_4$	90	1722	1720
[EMIM]$EtSO_4$	90	1719	1718
[BMIM]PF_6	90	1719	1718
[BMIM]BF_4	90	1719	1718

monomers MMA (1726 cm^{-1}) and GMA (1721 cm^{-1}) shows the higher polarity of GMA which is reflected in the k_p values ($k_{(GMA)} = 2067\ L \cdot mol^{-1} \cdot s^{-1}$ and $k_{(MMA)} = 1843\ L \cdot mol^{-1} \cdot s^{-1}$), too (cf. Table 3).

We also investigated the intermolecular interactions between the monomers and the ILs using either Monte-Carlo or dynamic simulations which apply a MMFF94 ("Merck Molecular Force Field") force field approach changed for the ILs.[29] The interactions of the monomers with the ILs are based on numerous H-bonds whose coordination is dependent on the chemical structure of the monomers. For the methacrylate monomers MMA, GMA and HPMA two different types of interactions with [EMIM]EtSO$_4$ were calculated: i) interactions between the C=O group of the monomer and the protons of the IL cation and ii) interactions between the protons of the monomer and the SO$_3$ group of the IL anion. The interaction i) causes a shift of the C=O vibration in the FTIR spectrum which was experimentally proved (Table 4) and also simulated by us.[29] The radial density distribution function analysis which was received from dynamic simulations of monomer and IL solutions indicates that interactions of type ii) occur more often than type i) interactions. The H-bonds of type i) were also observed for the carbonyl group of NPI. The interaction of the monomers NPI and St with the anions of the IL is less distinctive. The polar group which could mediate a specific interaction with the cations of the IL is missing at St. In the case of AN interactions with the IL cation via the nitrogen atom of AN can be found and additionally AN specifically interacts with the IL anion, too. Figure 4a exemplary shows the calculated energetically most favorable structure for MMA in [EMIM]EtSO$_4$. A distance in the range of 1.9 to 2.3 Å between the oxygen atom of the carbonyl group (MMA) and the hydrogen atom of the imidazolium cation was calculated. Besides this Lewis acid interaction between the C=O group and the extended imidazolium ring, numerous interactions between the SO$_3$ group and the hydrogen atoms of the MMA molecule were detected which possess an interatomic distance of 2.3 to 2.5 Å.

The energetically most favorable structure of St in [EMIM]EtSO$_4$ (Figure 4b) shows that styrene as anpolar monomer predominantly interacts with the anion (SO$_3$ group) of the IL. In contrast to MMA the distances between the interacting atoms of monomer and IL are bigger (>2.5 Å) and these interactions occur less

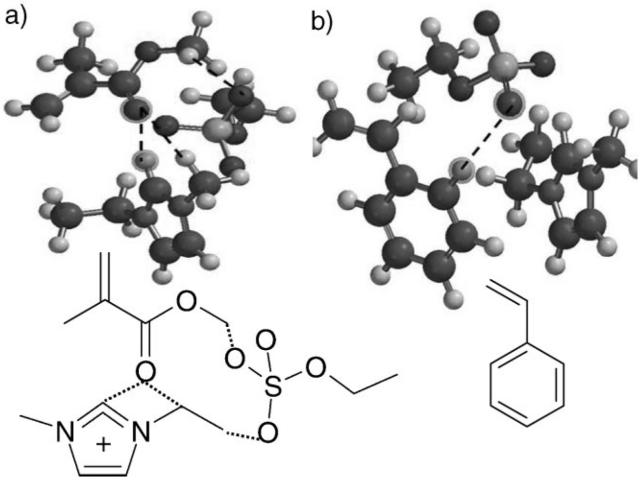


Figure 4.
Energetically most favorable structure for the systems a) MMA monomer in [EMIM]EtSO$_4$ and b) St monomer in [EMIM]EtSO$_4$, dotted line:H-bonds.[29]

often. Compared to the numerous H-bonds that were found for the IL solutions of the methacrylates, for example, for the system St/[EMIM]EtSO$_4$ H-bonds for only one atom pair can be detected.

Influence of k_t

Haddleton et al.[3] calculated the average termination rate coefficient k_t^m based on their PLP experiments for the MMA polymerization in [BMIM]PF$_6$. All experimental data for k_p (in [BMIM]PF$_6$,[3,4] [BMIM]BF$_4$,[4] [EMIM]HexSO$_4$[4] and [EMIM]EtSO$_4$[4]) and k_t^m (in [BMIM]PF$_6$[3]) in a temperature range of 25 and 40 °C are shown in Figure 5 in dependence of the volumetric IL fraction (c_{IL}) and the viscosity of the IL solutions.

With increasing IL concentration (reduction of MMA concentration), that means with increasing viscosity, the k_p values moderately increase whereas a very strong decrease can be found for k_t. The polymerization in the IL proceeds with an extremely decelerated termination reaction which leads to the strong increase of the molecular weights and the radical concentration and consequently k_p additionally is increased which results in an enhancement of the polymerization rate. By varying the solvent viscosity the influence of the IL should be controllable because a change in viscosity should affect k_p and k_t.

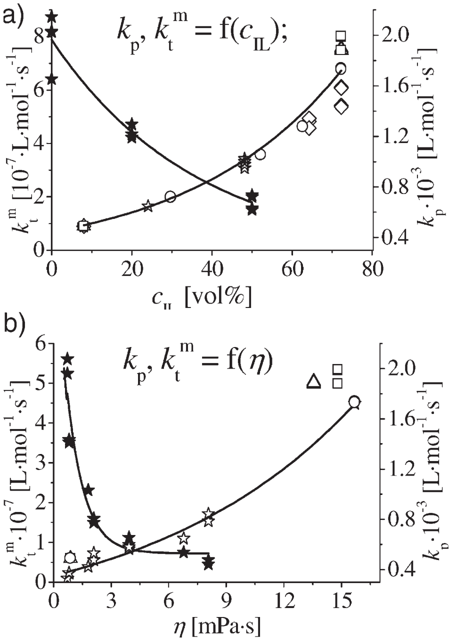


Figure 5.

Dependence of k_p (k_p in [BMIM]PF$_6$ (☆),[2] (○),[4] [BMIM]BF$_4$ (△),[2,4] [EMIM]HexSO$_4$ (◇)[4] and [EMIM]EtSO$_4$ (□)[4]) and k_t^m (k_t^m in [BMIM]PF$_6$ (★)[3]) of the MMA polymerization at $T = 25$ and 40 °C on a) the volumetric IL fraction (c_{IL}) and b) the initial viscosity of the reaction mixture (η)

In summary it can be said once more that the extraordinary strong solvent influence of the ILs on the free radical polymerization of polar monomers essentially arises from the increase of k_p which is on the one hand due to the formation of strong H-bonds between both monomer molecules and radical chain ends and the ILs and on the other hand due to the – in consequence of the high viscosity – very low termination rate coefficient k_t. The high viscosity of the IL as well as the during the course of reaction further increasing viscosity and therefore possible micro heterogeneities are responsible for the high molecular weights and polydispersities.

Reduction of the Specific Interactions

The number of H-bonds between both the monomer molecules and the growing polymer chains and the IL may be reduced by using microwave irradiation as the heating source for the polymerization or by decreasing the IL concentration in the reaction mixture which means by mixing the ILs with conventional organic solvents.

Microwave-Assisted Polymerization in ILs

The use of microwave reactor allows for a good control of the reaction parameters like e.g. pressure and reaction temperature. In addition, ILs are known to be good microwave absorbers due to their relatively high polarity. Figure 6 shows the comparison of heating curves of different solvents with constant microwave power.

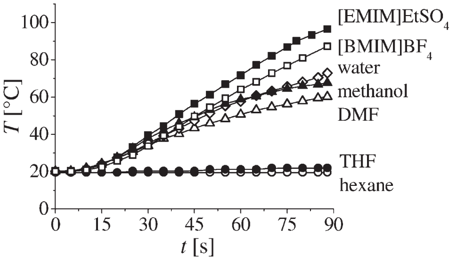


Figure 6.
Heating curves of different solvents (5 mL) with constant microwave power (100 W).

The interaction between microwave irradiation and polar components (here ILs) is based on the orientation of the molecules in the applied electric field. When the polarity of the electric field is reversed a reorientation of the molecules occurs. If the frequency is increased the orientation of the molecules is slower than the momentary field strength. Thus a heat loss (dissipation) occurs in the material. At the relaxation frequency the highest dissipation of energy can be observed. At frequencies above this relaxation frequency the interaction between the electric field and the polar molecules decreases due to the mass inertia. This strong interaction between the microwave irradiation and the ILs reduces the H-bonds between the monomer molecules as well as between the radical chain ends which results in a decrease of the rate constant of propagation k_p. Experimentally we have carried out a lot of polymerizations in [EMIM][EtSO$_4$] either using microwave irradiation or a heating block as heat source.[33] Figure 7

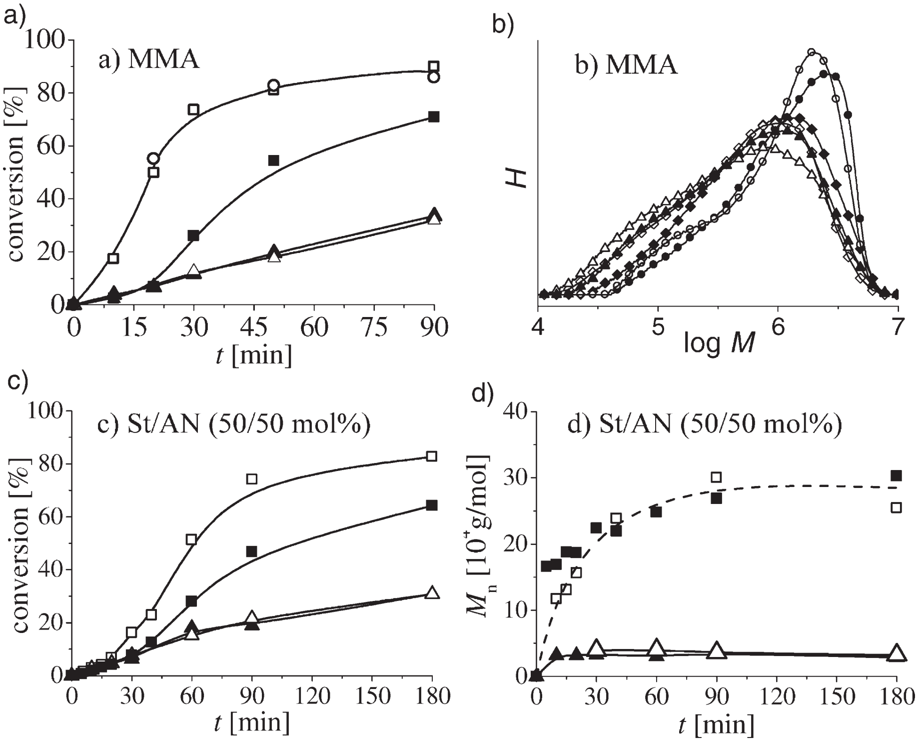


Figure 7.
a) Conversion and b) molecular weight distributions (MWDs) of the polymerization of MMA at 60 °C in DMF (microwave: ▲, heating block: △) and in [EMIM]EtSO$_4$ (microwave: ■, heating block: □, water bath: ○), MWDs: after 10 (●, ○), 30 (◆, ◇) and 90 (▲, △) min of reaction time, c) conversion and d) number average molecular weights M_n of the products of the St/AN (50/50 mol-%) polymerization at 60 °C in DMF (microwave: ▲, heating block: △) and in [EMIM]EtSO$_4$ (microwave: ■, heating block: □).

exemplary shows the expected decrease of the conversion for the polymerizations of MMA and St/AN (50/50 mol-%) under microwave irradiation. The molecular weights do not significantly change (Figure 7) because the viscosity and therefore k_t are not affected by microwave irradiation.

All the polymerizations in ILs[33] we carried out in a microwave reactor with variation of either the comonomers, the reaction temperature, the ILs or the initiators show a lower polymerization rate as a consequence of the reduction of the specific interactions between the IL, the monomer molecules and the polymer radicals. As expected, nearly the same very high molecular weights were found because at constant viscosity k_t leads to comparable molecular weights.

Influence of the IL Concentration

For the variation of the IL concentration a DMF/[EMIM]EtSO4 solvent mixture is used for the polymerization. The viscosity in dependence of the IL concentration of the solvent mixture was experimentally determined (Figure 8a).

The reduction of the IL concentration does not only lead to a decrease of the number of H-bonds (concentration effect) and therefore to a decrease of the k_p values (Figure 5a), it also results in a lowered viscosity of the reaction mixture. Decreasing the viscosity induces lower molecular weights because the termination reaction is accelerated and thus k_t increases.

In the following the dependence of the conversions and the number average molecular weights M_n (Figure 8d) on the IL concentration is described at the example of the homopolymerizations of MMA and AN as well as the copolymerizations of MMA/AN (90/10 mol-%), MMA/St (90/10 mol-%) (Figure 8c) and St/AN (50/50 mol-%) (Figure 8b) after a reaction time of 30 min at a reaction temperature of

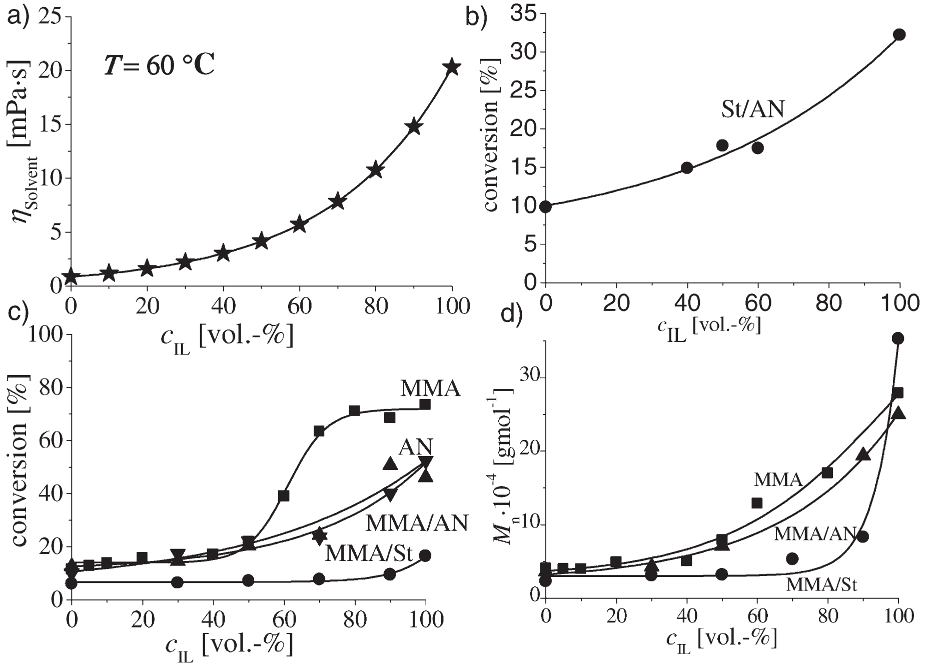


Figure 8.

a) Viscosity of the solvent mixture IL/DMF $\eta_{solvent}$ (★) as function of the volume fraction of the c_{IL}, b) conversion of the St/AN (50/50 mol-%) copolymerization in dependence on c_{IL} (●), c) conversion and d) number average molecular weights M_n after $t = 30$ min of the polymerizations of MMA (■), AN (▼), MMA/AN (90/10 mol-%) (▲) and MMA/St (90/10 mol-%) (●) as function of the volumetric IL fraction c_{IL} at $T = 60$ °C.

T = 60 °C. An effective influence of the IL especially on the polar monomers is only visible at high IL concentrations.

In Figure 9 the MWDs for PMMA (Figure 9a) and St/AN copolymer (synthesized with 80 mol-% AN in the initial comonomer mixture (Figure 9b) received after a reaction time of 30 min with variation of the IL volume fraction in the IL/DMF solvent mixture are shown. With decreasing IL content in the solvent mixture the high molecular weight fraction in the polymers decreases. Bimodal MWDs can be observed for PMMA when it is produced using a solvent mixture containing 40 to 100 vol.-% of IL. The location of the high molecular weight peak stays constant in this range of the IL concentration but loses height with decreasing IL content. As expected the chain length increases on the one hand due to the increase of k_p and on the other hand due to the deceleration of the termination reaction (reduction of k_t) with increasing IL concentration in the solvent mixture and thus with increasing viscosity.

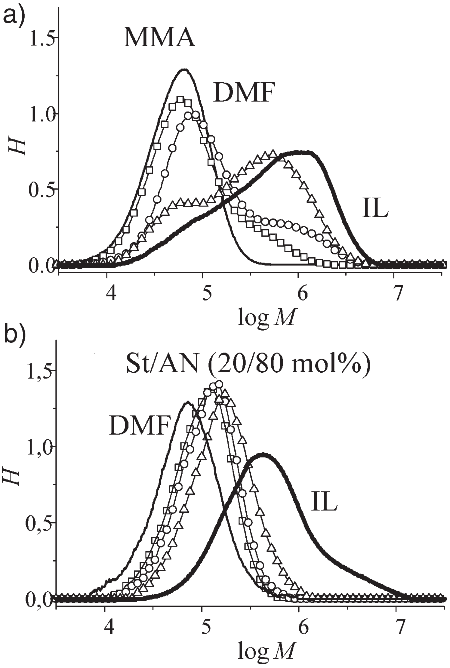


Figure 9.
Molecular weight distributions for PMMA and St/AN) (20/80 mol-% in the initial comonomer mixture) synthesized by polymerization in IL/DMF solvent mixtures with varied IL volume fractions $c_{IL} = 0$ vol.-% (—), 40 vol.-% (□), 50 vol.-% (○), 60 vol.-% (△), 100 vol.-% (▬), $t = 30$ min, $T = 60$ °C.

The use of diluted IL solutions rapidly decreases the solvent influence of the IL on the polymerization that means the rate of polymerization and the molecular weights rapidly decrease because of the drastic reduction of the number of H-bonds and the decreasing viscosity of the reaction mixture. In[13,14] we investigated the variation of the viscosity either by dilution of the IL or by increasing the reaction temperature in detail.

Influence of the Reaction Temperature

An intense reduction of the viscosity of the IL which is used as solvent can also be obtained by working at higher reaction temperatures. The viscosity of [EMIM]EtSO$_4$ was experimentally determined in dependence on the temperature and is shown in Figure 10. The resulting ARRHENIUS-ANDRADE equation is: $\ln \eta = -8.38 + 3766/T$.

In Figure 11 the conversion time curves of the MMA polymerization in [EMIM]EtSO$_4$ and in DMF at the reaction temperature of $T = 60$ and 80 °C are comparatively depicted. With increasing temperature the radical concentration and therefore the conversion increases. The

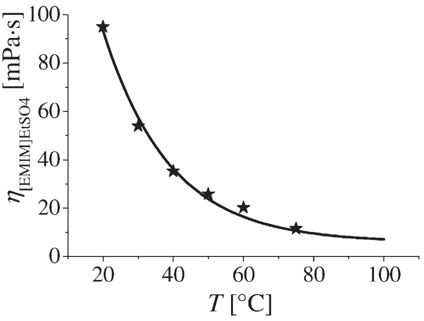


Figure 10.
Viscosity of the IL [EMIM]EtSO$_4$ $\eta_{[EMIM]EtSO4}$ (experimentally determined (★) and calculated with $\ln \eta = -8.38 + 3766/T$ (—)) in dependence of the temperature.

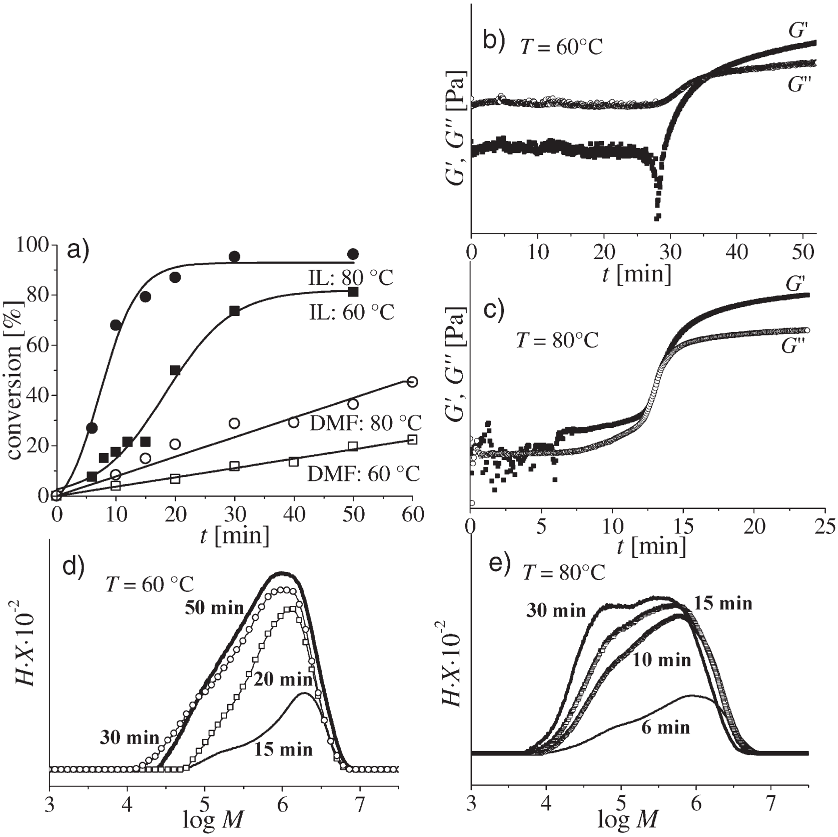


Figure 11.

a) Conversion time curves of the MMA polymerization at 60 °C in [EMIM]EtSO$_4$ (■) and DMF (□) and at 80 °C in [EMIM]EtSO$_4$ (●) and DMF (○); rheological online measurement of G' and G'' of the MMA polymerization in [EMIM]EtSO$_4$ at b) $T = 60$ °C and c) $T = 80$ °C; time dependent conversion standardized molecular weight distributions at d) $T = 60$ °C and e) $T = 80$ °C.

deviation of k_p between the reactions in IL and those in DMF becomes insignificantly smaller with increasing temperature because the activation energy of propagation is 4.3 kJ $\cdot$ mol^{-1} lower when MMA is polymerized in the IL ($c_{MMA} = 20$ vol.-%) instead of in bulk as we have already reported in.[4] With the ARRHENIUS parameters for the MMA polymerization in IL given in Table 3 at 60 °C $k_p = 2759$ L $\cdot$ mol $\cdot$ s^{-1} can be calculated which means that it is 4.7 times higher than k_p for the bulk polymerization whereas at 80 °C only a 4.3 times higher k_p can be found in the IL ($k_p = 3995$ L $\cdot$ mol $\cdot$ s^{-1}). Already at the beginning of the MMA polymerization the viscosity of the reaction mixture is relatively high, especially at T = 60 °C, and therefore the k_t value is very small which leads to the formation of very long polymer chains. With increasing the conversion the high-molecular chains form entanglement networks which increasingly limit the free motion of the monomer molecules. The diffusion control of the termination reaction is overlaid by the diffusion controlled propagation reaction. The system stops when the limit conversion is reached. Polymerizations with rheological online control show a gel point after 30 min at T = 60 °C (Figure 11b) or after 12 min at T = 80 °C (Figure 11c) which can be

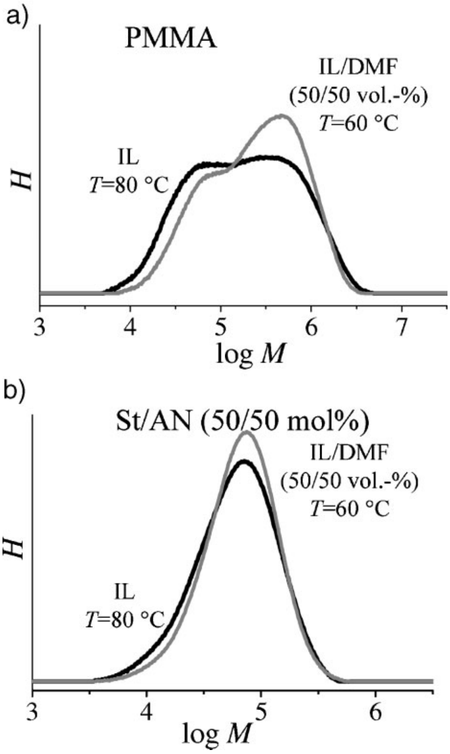


Figure 12.
Comparison of the molecular weight distributions of polymers synthesized in a IL/DMF (50/50 vol.-%) mixture and at elevated reaction temperature in pure IL, respectively, solvent viscosity is almost constant,; a) MMA polymerization in [EMIM]EtSO$_4$ ($T = 80$ °C: $X = 96\%$) and [EMIM]EtSO$_4$/DMF (50/50 vol%; $T = 60$ °C: $X = 78\%$); b) St/AN(50/50 mol-%) copolymerization in [EMIM]EtSO$_4$ ($T = 80$ °C: $X = 76\%$) and [EMIM]EtSO$_4$/DMF (50/50 vol%; $T = 60$ °C: $X = 16\%$).

ascribed to the entanglement networks of the long chain material. The reaction solution becomes a highly viscous gel after 30 min and 12 min, respectively, in which MMA is increasingly enclosed. The result is the observed reduction of the chain lengths until a limit conversion of about 80% is reached after 35 min ($T = 60$ °C) and 90% after 12 min ($T = 80$ °C), respectively (Figure 11e).

An interesting question is how the molecular weight distributions (MWDs) differ from each other when almost the same viscosity of the solvent (IL) is adjusted either by dilution of the IL with DMF or by an increased reaction temperature. In Figure 12 the MWDs for the MMA polymerization (Figure 12a) and the St/AN (50/50 mol-%) copolymerization (Figure 12b) in a [EMIM]EtSO$_4$/DMF solvent mixture containing 50 vol.-% IL at a reaction temperature of 60 °C are compared to the MWDs of both polymerizations carried out at 80 °C in the pure IL. The molecular weight distributions of the MMA as well as the St/AN polymerization do not significantly differ from each other that means the viscosity and therefore k_t are responsible for the development of the molecular weights.

Conclusion

An effective influence of the ILs as solvents for the free radical polymerization can only be observed for polar monomers that are soluble in the IL. This solvent influence is noticeable in the strong enhancement of the polymerization rate and the very high, mostly broadly distributed molecular weights. H-bonds between the monomer molecules as well as the growing radical chains and the cations and anions of the IL are responsible for the increase of the propagation rate coefficient k_p. In a microwave reactor these specific interactions can be disturbed. Thus the influence of the IL on the free radical polymerization is diminished. The high viscosities of the ILs as well as the increasing viscosity of the reaction mixture during the polymerization reaction and therefore possible micro heterogeneities are responsible for the high molecular weights and mostly high polydispersities.

We can conclude that the most suitable application of ILs as solvent for the free radical polymerization is the acceleration of the reaction rate at elevated reaction temperatures. At a reaction temperature of 80 °C already after about 20 min a limit conversion of ~90% and almost a doubling of the molecular weights are reached in comparison to polymerizations carried out in organic solvents. In Figure 11 the

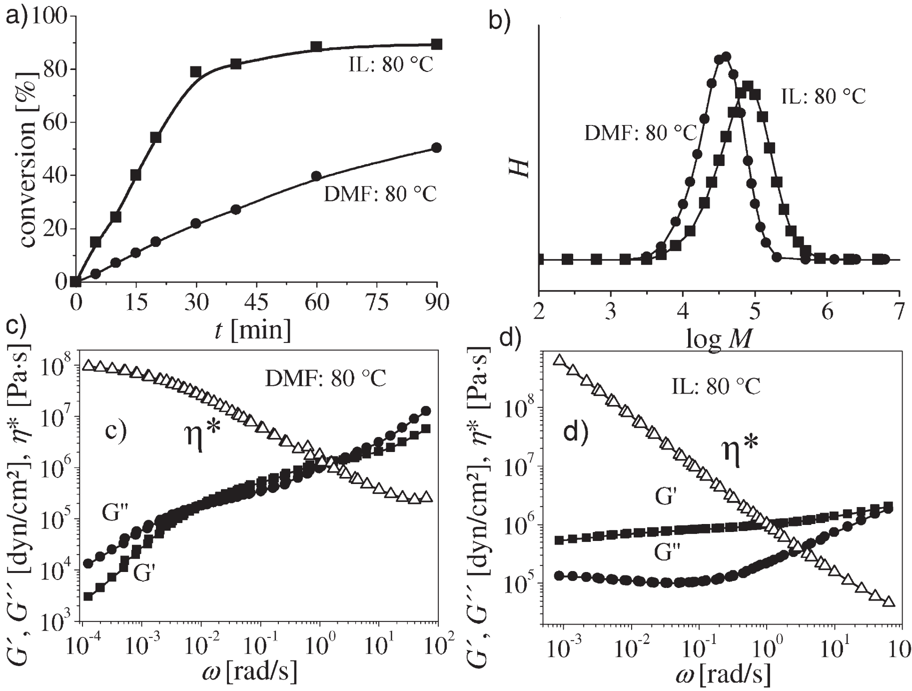


Figure 13.

Copolymerization of St/AN (50/50 mol-%) at 80 °C in the solvents DMF and [EMIM]EtSO$_4$. a) Conversion time curves, b) MWDs received after $t = 35$ min, $X_{IL} = 88.3\%$, t = 90 min, $X_{DMF} = 50.3\%$; storage modulus G'(■), loss modulus G''(●) and complex viscosity η^* (△) in dependence of the frequency ω for c) St/AN from DMF solution and d) St/AN from [EMIM]EtSO$_4$ solution, temperature range: 125–165 °C, reference temperature: 125 °C.

conversion time behavior as well as the time dependent development of the molecular weights for the MMA polymerization in the solvents DMF and [EMIM]EtSO$_4$ at T = 80 °C are shown.

Figure 13a shows at the example of the St/AN (50/50 mol-%) copolymerization the time dependent conversion development using [EMIM]EtSO$_4$ and DMF as solvents at a reaction temperature of 80 °C. The molecular weight distributions of the copolymers obtained after a reaction time of 35 min with conversions of either 88.3% in the IL or after a reaction time of 90 min 50.3% in DMF are represent in Figure 13b. The copolymer composition with an AN fraction of ~45 mol-% in both solvents almost matches the azeotropic composition (St/AN = 61.5/38.5 mol-%). Figure 13c and 13d document the varying rheological behavior of the copolymers which only differ in the solvent used for the polymer synthesis and therefore basically in their molecular weights. The storage (G') and the loss modulus (G'') of the copolymer produced in the IL are nearly independent of the frequency for $\omega < 10^{-1}$ rad · s^{-1} which can be explained by the entanglement of the long polymer chains.

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